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European Patent Office  
Office européen des brevets



(11)

**EP 1 405 933 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
**07.04.2004 Bulletin 2004/15**

(51) Int Cl.7: **C23C 22/34, C23C 22/50,  
C23C 22/53, B05D 3/10**

(21) Application number: **02736073.4**

(86) International application number:  
**PCT/JP2002/005860**

(22) Date of filing: **12.06.2002**

(87) International publication number:  
**WO 2002/103080 (27.12.2002 Gazette 2002/52)**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **15.06.2001 JP 2001182365  
15.06.2001 JP 2001182366  
06.09.2001 JP 2001269995**

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(54) **TREATING SOLUTION FOR SURFACE TREATMENT OF METAL AND SURFACE TREATMENT METHOD**

(57) The present invention is the method for surface treatment of a metal material containing iron and/or zinc, comprising component (A) and component (B);

(A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,

(B) a compound containing fluorine as a supplying source of HF,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of 0.06

$\leq K \leq 0.18$ , and the concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si is within the region of 0.05 to 100 m mol/L. To the treating solution for surface treatment, at least one compound containing at least one metal element selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn can be blended.

It is possible to form a surface treated film which is superior at corrosion resistance after coated on the surface of a metal containing iron or zinc, in the solution which does not contain harmful component to the environmental.

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**Description**

FIELD OF THE INVENTION

**[0001]** The present invention relates to a composition for metal surface treatment which make it possible to form a surface treated film having excellent corrosion resistance after coated on the surface of a metal containing iron and/or zinc, a treating solution for metal surface treatment, a method for metal surface treatment and a metal material having excellent corrosion resistance obtained by using said treating solution.

BACKGROUND OF THE INVENTION

**[0002]** As the method to form on metal surface a surface treated film having excellent corrosion resistance after coated, a zinc phosphate process and a chromate process are currently used as an ordinary method. According to the zinc phosphate process, it is possible to form a film having excellent corrosion resistance on the surface of steel such as cold rolled steel plate, zinc plated steel plate and a kind of aluminum alloy. However, at the zinc phosphate process, the generation of sludge, which is the byproduct of the reaction can not be avoided, further according to the kind of aluminum alloy, the sufficient corrosion resistance after coated can not be obtained. While, in the case of aluminum alloy, it is possible to obtain sufficient properties after coated by a chromate process. But, concerning the recent environmental regulation, the chromate process which contains harmful hexavalent chrome in the treated solution is becoming to be evaded. As the method for metal surface treatment, which does not contain harmful component in the treated solution, various methods were proposed.

**[0003]** For example, in JP2000-204485A publication, a compound containing nitrogen atom having a lone electron-pair or a non-chrome coating agent for metal surface treatment containing said compound and zirconium compound are disclosed. This method makes it possible to obtain a surface treated film which is excellent at corrosion resistance and adhesion after coated by coating above mentioned coating agent, and yet, in this method, harmful hexavalent chrome is not contained. However, in the case of said method, the metal material which can be treated is limited to aluminum alloy alone, further, it is difficult to be applied to a body having complex structure, because the surface treated film is formed by coating and drying.

**[0004]** Further, as the method to form a metal surface treated film having excellent adhesion and corrosion resistance after coated by chemical reaction, various methods are disclosed, for example, JP56-136978A publication, JP9-25436A publication or JP9-31404A publication. However, in these cases, the metal material which can be treated is limited to the aluminum alloy alone. However, since the aluminum alloy has originally excellent corrosion resistance, the actual uses are limited to the narrow use such as aluminum DI can.

**[0005]** Furthermore, in JP2000-199077A publication, the method to form a metal surface treated film having excellent corrosion resistance and adhesion after coated is disclosed, and the important point of this method is to use a surface treating agent composed of metal acetylacetonate and water soluble inorganic titanium compound or water soluble inorganic zirconium compound. By this method, the kinds of metal material which can be treated are extended to magnesium, magnesium alloy, zinc and zinc plated alloy other than aluminum alloy. However, by this method, it is difficult to form a sufficient amount of surface treated film on a surface of iron such as cold rolling steel, that is, this method can not be expected at all to have an aimed effect on a surface of iron.

**[0006]** Still further, in JP5-195244 A publication, the method for metal surface treatment by chrome free coat type acid composition is disclosed. This method for metal surface treatment is characterized as follows. That is, aqueous solution containing component which can be a film having excellent corrosion resistance is coated over the surface of metal, then baked and dried without rinsing so as the film to be fixed. This method is not accompanied with any chemical reaction, therefore, by this method, it is possible to form a film on the surface of metal such as zinc plated steel plate, cold rolled steel plate or aluminum alloy. However, same as to the invention disclosed in above mentioned JP2000-204485A publication, since the film is generated by coating and drying, this method can not be applied to a body having complex structure.

**[0007]** As mentioned above, according to the prior arts, it was impossible to perform surface treatment excels in corrosion resistance and adhesion on various metal materials having broad extension from iron material such as cold milling steel, zinc material to light metal such as aluminum alloy, without containing harmful component to the environment and not generating waste sludge.

DISCLOSURE OF THE INVENTION

**[0008]** The object of the present invention is to provide a composition for surface treatment which make it possible to form a surface treated film having excellent corrosion resistance after coated on the surface of a metal containing iron and/or zinc, a treating solution for metal surface treatment, a method for metals surface treatment and a metal

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material having excellent corrosion resistance obtained by using said treating solution.

**[0009]** The present invention is a composition for surface treatment of a metal containing iron and/or zinc, which comprises component (A) and component (B);

- 5 (A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.06 \leq K \leq 0.18$ .

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**[0010]** Further, the present invention is a composition for surface treatment of a metal containing iron and/or zinc, which comprises component (A), component (B) and component (C);

- 15 (A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,  
(C) a compound containing at least one metal element selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.03 \leq K \leq 0.167$ .

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**[0011]** Furthermore, the present invention is a treating solution for surface treatment of a metal containing iron and/or zinc, which comprises component (A) and component (B);

- 25 (A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.06 \leq K \leq 0.18$ , and the concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si is within the region of 0.05 to 100 m mol/L.

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**[0012]** Still further, the present invention is a treating solution for surface treatment of a metal containing iron and/or zinc, which comprises component (A), component (B) and component (C);

- 35 (A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,  
(C) a compound containing at least one metal element selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.03 \leq K \leq 0.167$ , and the concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si is within the region of 0.05 to 100 m mol/L. It is desirable to adjust the blending amount of compound of component (C) in the solution for surface treatment of a metal to the sufficient amount to make the free fluorine ion concentration in treating solution measured by fluorine ion meter smaller than 500 ppm.

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**[0013]** And to each above mentioned treating solution for surface treatment of a metal, at least one compound selected from the group consisting of  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HMnO}_4$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{WO}_4$ ,  $\text{H}_2\text{MoO}_4$  and salts of these oxygen acids can be added. Further, to each above mentioned treating solution for surface treatment of a metal, at least one kind of surface active agent selected from the group consisting of nonion surface active agent, anion surface active agent and cation surface active agent can be added, and can adjust pH within the range of 2 to 6. Furthermore, to each above mentioned treating solution for surface treatment of a metal, at least one kind of polymer component selected from the group consisting of water soluble polymer compound and water dispersible polymer compound can be added.

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**[0014]** Yet further, the present invention is the method for surface treatment of a metal containing iron and/or zinc characterizing, the cleaned metal surface by previous degreasing treatment is contacted with any one of above mentioned treating solutions for surface treatment of a metal. And, the present invention is the method for surface treatment of a metal containing iron and/or zinc characterizing, using the cleaned metal surface by previous degreasing treatment

as a cathode and treating by electrolysis in any one of above mentioned treating solutions for surface treatment of a metal. Further, in the case when the treating solutions for surface treatment of a metal to which above mentioned surface active agent is blended and whose pH is adjusted to the range of 2 to 6, it is possible to carry out the degreasing and cleaning treatment and surface film forming treatment.

**[0015]** More over, the present invention is the metal material having excellent corrosion resistance, possessing surface treated film layer on the surface of iron metal material, which is formed by above mentioned method for surface treatment, composed of oxide and or hydroxide of at least one kind of metal element selected from the group consisting of Ti, Zr, Hf and Si, and the amount of said surface treated film layer is over than 30mg/m<sup>2</sup> by converted amount to said metal elements. And the present invention is the metal material having excellent corrosion resistance, possessing surface treated film layer composed of oxide and or hydroxide of at least one kind of metal element selected from the group consisting of Ti, Zr, Hf and Si formed by above mentioned method for surface treatment on the surface of zinc metal material, and the amount of said surface treated film layer is over than 20mg/m<sup>2</sup> by converted amount to said metal elements.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

**[0016]** The present invention relates to a technique to form surface treated film having excellent corrosion resistance after coated on the surface of a metal containing iron and/or zinc by chemical or electrochemical reaction. In the present invention, a metal containing iron and/or zinc means the metal material consisting of iron and/or zinc such as steel plate, zinc plated steel plate. Concretely, for example, iron metal material such as cold rolled steel plate, hot rolling steel plate, cast iron or sintered steel can be mentioned. The present invention can be applied not only to the metal material of iron or zinc or to the combined metal material of iron and zinc, but also to the combined metal material composed of a metal material containing at least one of iron or zinc and a metal material such as magnesium alloy or aluminum alloy, for instance, the combined metal material composed of steel plate, zinc plated steel plate and aluminum alloy or magnesium alloy. More over, can be applied to the sole metal material e.g. magnesium alloy or aluminum alloy.

**[0017]** The composition for surface treatment of a metal containing at least one of iron or zinc of the present invention contains component (A) and component (B). As the concrete example of the compound of component (A) containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si, for example, TiCl<sub>3</sub>, TiCl<sub>4</sub>, Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ti(SO<sub>4</sub>)<sub>2</sub>, Ti(NO<sub>3</sub>)<sub>4</sub>, H<sub>2</sub>TiF<sub>6</sub>, salt of H<sub>2</sub>TiF<sub>6</sub>, TiO, Ti<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, TiF<sub>4</sub>, ZrCl<sub>4</sub>, Zr(SO<sub>4</sub>)<sub>2</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>, H<sub>2</sub>ZrF<sub>6</sub>, salt of H<sub>2</sub>ZrF<sub>6</sub>, ZrO<sub>2</sub>, ZrF<sub>4</sub>, HfCl<sub>4</sub>, Hf(SO<sub>4</sub>)<sub>2</sub>, H<sub>2</sub>HfF<sub>6</sub>, salt of H<sub>2</sub>HfF<sub>6</sub>, HfO<sub>2</sub>, HfF<sub>4</sub>, H<sub>2</sub>SiF<sub>6</sub>, salt of H<sub>2</sub>SiF<sub>6</sub>, Al<sub>2</sub>O<sub>3</sub>(SiO<sub>2</sub>)<sub>3</sub> or SiO<sub>2</sub> can be mentioned. These compounds can be used together with.

**[0018]** And, as the concrete example of the compound containing fluorine as a supplying source of HF, hydrofluoric acid can be used, and besides hydrofluoric acid, fluorine compound such as H<sub>2</sub>TiF<sub>6</sub>, TiF<sub>4</sub>, H<sub>2</sub>ZrF<sub>6</sub>, ZrF<sub>4</sub>, H<sub>2</sub>HfF<sub>6</sub>, HfF<sub>4</sub>, H<sub>2</sub>SiF<sub>6</sub>, HBF<sub>4</sub>, NaHF<sub>2</sub>, KHF<sub>2</sub>, NH<sub>4</sub>HF<sub>2</sub>, NaF, KF, NH<sub>4</sub>F can be mentioned. These compounds can be used together with.

**[0019]** To the composition for surface treatment of a metal of the present invention, component (C) can be further blended besides above mentioned components (A) and (B). Component (C) is the compound containing at least one metal element selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn. These compounds are oxide, hydroxide, chloride, sulfate, nitrate or carbonate of above mentioned elements, and as the concrete example, AgCl, AlCl<sub>3</sub>, FeCl<sub>2</sub>, FeCl<sub>3</sub>, MgCl<sub>2</sub>, CuCl<sub>2</sub>, MnCl<sub>2</sub>, ZnCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, Ag<sub>2</sub>SO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, MgSO<sub>4</sub>, CuSO<sub>4</sub>, MnSO<sub>4</sub>, ZnSO<sub>4</sub>, NiSO<sub>4</sub>, CoSO<sub>4</sub>, AgNO<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> can be mentioned. These compounds can be used together with.

**[0020]** At the actual use for surface treatment of a metal, the above mentioned composition of the present invention is used by diluting it with water or by dissolving it into water. Namely, the composition is prepared as the treating solution for surface treatment of a metal, and then is used. At the preparation of the treating solution for surface treatment of a metal, water is added to the composition for surface treatment of a metal and adjust the concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si to be within the region of 0.05 to 100 m mol/L. The treated film can be formed on the surface of metal by contacting metal material to be treated with the treating solution for surface treatment of a metal.

**[0021]** The metal elements of Ti, Zr, Hf and Si in the compound of component (A) are existing as H<sub>2</sub>MF<sub>6</sub> (wherein M is at least one metal element selected from the group consisting of Ti, Zr, Hf and Si) in aqueous solution containing sufficient amount of HF. When the mole concentration of fluorine ion is smaller than six times as much as concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si, these metal elements are existing as salts of said H<sub>2</sub>MF<sub>6</sub> and other acids. While, between H<sub>2</sub>MF<sub>6</sub> and HF, following chemical equilibrium comes into existence.



**[0022]** And, when the metal material to be treated is soaked into the composition for surface treatment of a metal of the present invention, for example, in the case of the metal material is iron, HF is consumed by etching reaction of



That is, by the etching reaction shown by the reaction formula (2) HF is consumed and the equilibrium of (1) is forwarded to the right, then  $\text{MO}_2$ , which is the main component of surface treated film obtained by the present invention is formed. The obtained film is the oxide and/or hydroxide of metal element M. At the present time, the detailed investigation of this film is not yet carried out, however, the effect for the improvement of corrosion resistance and adhesion is not influenced by the feature of the film, namely, whether the film is amorphous or crystalline substance.

**[0023]** The pH of the treating solution for surface treatment of a metal of the present invention is not restricted, however, at the occurrence of etching reaction of metal material to be treated, the stability of treating solution is taken into consideration, desirable pH is 2 to 6 and more desirable pH is from 3 to 5.

**[0024]** In the case when the composition for surface treatment or treating solution for surface treatment contains components (A) and (B) and does not contain component (C), it is necessary that the ratio  $K = A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si and mole weight B which when total F in above mentioned fluorine containing compound is converted to HF is within the range of  $0.06 \leq K \leq 0.18$  to form a film having excellent corrosion resistance and adhesion by reaction formulae (1) and (2). When K is larger than 0.18, although it is possible to form enough amount of film to obtain corrosion resistance and adhesion, the stability of the composition for surface treatment or the treating solution for surface treatment is spoiled and the continuous operation becomes difficult. And when K is smaller than 0.06, since it becomes difficult to forward the equilibrium of (1) to the right, the film having sufficient amount to obtain corrosive resistance and adhesion can not be formed in a short time. Especially, when K is small, since the film formation on iron material is very difficult, it becomes difficult to form a surface treated film having excellent corrosion resistance after coated by chemical or electrochemical reaction on the surface of combined metal material composed of steel plate, zinc plated steel plate and aluminum alloy or magnesium alloy in a short time.

**[0025]** To the composition for surface treatment or treating solution for surface treatment of the present invention component (C) can be further blended besides above mentioned components (A) and (B). By blending component (C), at least one metal element in compound of component (C) selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn forms complex fluorine compound with HF or fluorine ion in treating solution and forwards the equilibrium of (1) to the right and effects to promote the film forming reaction. By adding at least one element which generates complex fluorine compound selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn, the concentration of free fluorine ion can be regulated, and the reactivity of the treating solution for surface treatment of the present invention to the metal material to be treated can be voluntarily regulated. As the method for easy monitoring of reactivity, a method to measure the concentration of free fluorine ion using a fluorine ion meter can be used. The concentration of free fluorine ion is desirably less than 500 ppm and more desirably less than 300 ppm. When the concentration of free fluorine ion is over than 500 ppm, the concentration of HF in the treating solution becomes high, therefore the equilibrium of (1) is hard to be forwarded to the right and it is difficult to form the enough amount of film to obtain corrosive resistance and adhesion.

**[0026]** In the case when the composition for surface treatment or treating solution for surface treatment contains components (A), (B) and (C), it is necessary that above mentioned ratio K is within the range of  $0.03 \leq K \leq 0.167$  to form a film having excellent corrosion resistance and adhesion by reaction formulae (1) and (2). When K is larger than 0.167, although it is possible to form enough amount of film to obtain corrosion resistance and adhesion in a short time, in the case when component (C) is added, the stability of the composition for surface treatment or the treating solution for surface treatment is spoiled and the continuous operation becomes difficult. And when K is smaller than 0.03, since it becomes difficult to forward the equilibrium of (1) to the right, the film having sufficient amount to obtain corrosive resistance and adhesion can not be formed. Especially, when K is small, since the film formation on an iron material is very difficult, it becomes impossible to form a surface treated film having excellent corrosion resistance after coated by chemical or electrochemical reaction on the surface of combined metal material composed of steel plate, zinc plated steel plate and aluminum alloy or magnesium alloy in a short reaction time.

**[0027]** The present invention is to form the surface treated film on a metal surface using equilibrium reaction between  $\text{H}_2\text{MF}_6$  and HF. Accordingly, it is necessary that the concentration of compound (in the case when more than 2 kinds of said compounds are used, is the total mole concentration) containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si of component (A) in treating solution for surface treatment of a metal is the concentration to make regulate the total mole concentration of metal elements of Ti, Zr, Hf and Si within the region of 0.05 to 100 m mol/L. When the total mole concentration as metal element is within the range of 0.05 to 100 m mol/L, the metal element can be used by alone or can be used together with. If the total mole concentration is less than 0.05 m

mol/L, since the concentration of above mentioned metal element, which is the component for film, is remarkably small, it is difficult to form the film of enough amount to obtain adhesion and corrosion resistance. Further, even if the total mole concentration is larger than 100 m mol/L, although the film forms, the remarkable improvement of adhesion and corrosion resistance can not be expected, and is disadvantageous from the economical view point.

**[0028]** HF, which is the component in the treating solution for surface treatment of the present invention, acts as mentioned above, and more over acts to maintain the component of material to be treated solved out by etching reaction as the fluorine complex in the treating solution. By said action of HF, the treating solution for surface treatment of the present invention does not generate sludge. Further, in the case when the treating amount of metal material to be treated is remarkably large to the amount of treating solution, it is possible to add acids other than HF or chelating agent which make possible to chelate metal ions solved out from the metal material to be treated, for the purpose to solubilize the solved out component of material to be treated. As an example of acid which can be used in the present invention, inorganic acid such as sulfuric acid or hydrochloric acid, or organic acid such as acetic acid, oxalic acid, tartaric acid, citric acid, succinic acid, gluconic acid or phthalic acid can be mentioned.

**[0029]** In the treating solution for surface treatment of the present invention, at least one compound selected from the group consisting of  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HMnO}_4$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{WO}_4$ ,  $\text{H}_2\text{MoO}_4$  and salts of these oxygen acid can be added. Said one compound selected from the group consisting of these oxygen acid and salts of these oxygen acid acts as an oxidant to the metal material to be treated and promotes the film forming reaction of the present invention.

**[0030]** The adding concentration of above mentioned at least one compound selected from the group consisting of  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HMnO}_4$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{WO}_4$ ,  $\text{H}_2\text{MoO}_4$  and salts of these oxygen acid is not restricted, however, in the case when it is used as an oxidant, the enough effect can be expected at the adding amount of 10-5000 ppm. Further, as represented by  $\text{HNO}_3$ , in the case when said acids act as the acid to maintain the etched component of metal material to be treated in the treating solution, it is possible to increase the adding amount if necessary.

**[0031]** The method for surface treatment of the present invention can be illustrated as follows. Namely, the surface is treated by degreasing treatment according to the ordinary method, and the cleaned metal material to be treated is contacted to the treating solution for surface treatment. Accordingly, the film composed of oxide and or hydroxide of at least one kind of metal element selected from the group consisting of Ti, Zr, Hf and Si is deposited and the surface treated film layer having good adhesion and corrosion resistance is formed. As the substantial method for this contacting process, any kind of process e.g. spray treatment, immersion treatment or pouring treatment can be used, and the properties of the product is not influenced by the treating method. From the chemical view point, it is difficult to obtain the hydroxide of above mentioned metal as a pure hydroxide, and in general, the form the oxide of above mentioned metal to which hydrated water is attached is considered to be in the category of hydroxide. Therefore, the hydroxide of said metal finally becomes the oxide by heating. The structure of the surface treated layer of the present invention is considered to be mixed state of oxide and hydroxide when dried by ordinary temperature or by low temperature after surface treatment. And, in the case when dried by high temperature after surface treatment, the structure of the surface treated layer is considered to be composed by oxide alone or oxide rich.

**[0032]** In the present invention, the using condition of treating solution for surface treatment is not restricted. The reactivity of the treating solution for surface treatment of the present invention can be voluntarily regulated by changing  $K=A/B$ , which is the ratio between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine in fluorine containing compound of component (B) is converted to HF. Further, the reactivity can be also voluntarily regulated by adding at least one element which forms complex fluorine selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn in component (C). Therefore, the treating temperature and treating time can be voluntarily changed by combining with the reactivity of treating solution.

**[0033]** Further, to each above mentioned treating solution for surface treatment of a metal, at least one kind of surface active agent selected from the group consisting of nonion surface active agent, anion surface active agent and cation surface active agent can be added, and can adjust pH within the range of 2 to 6. At the surface treatment of a metal material using this treating solution for surface treatment, the good film can be formed without previous degreasing and cleaning treatment of the metal material to be treated. That is, this treating solution for surface treatment of a metal can be used simultaneously as a surface treating agent and a degreasing agent.

**[0034]** To the treating solution for surface treatment of the present invention, at least one kind of polymer component selected from the group consisting water soluble polymer compound and water dispersible polymer compound can be added. The metal material whose surface is treated by the treating solution for surface treatment of the present invention has sufficient corrosion resistance, however, if the additional function, lubricating ability is required, a polymer compound which meets to the requirement can be selected and added. Thus the physical property of the treated film can be modified. As the concrete example of above mentioned water soluble polymer compound and water dispersible polymer, for example, polyvinyl alcohol, poly(meta)acrylic acid, copolymer of acrylic acid and methacrylic acid, copolymer of ethylene with acrylic monomer such as (meta)acrylic acid or (meta)acrylate, copolymer of ethylene with vinylacetate, polyurethane, amino denatured phenolic resin, polyester resin and epoxy resin, which are normally used for

the surface treatment of a metal, can be mentioned.

**[0035]** Further, in the case when the surface treated film layer is formed using electrolysis method, using the cleaned metal surface by previous degreasing treatment as a cathode, and treated by electrolysis using a surface treating solution containing a compound which contains at least one metal element selected from the group consisting of Ti, Zr, Hf and Si of component (A) and a fluorine containing compound and/or inorganic acid as a supplying source of HF for component (B), then rinsed by water. As the inorganic acid to be used, at least one acid selected from the group consisting of nitric acid, sulfuric acid, acetic acid and hydrochloric acid can be mentioned.

**[0036]** At least one metal element selected from the group consisting of Ti, Zr, Hf and Si supplied from component (A) and HF and/or inorganic acid supplied from component (B) are forming soluble salt in aqueous acid solution and dissolved. When a metal material is set up as a cathode and treated by electrolysis, reductive reaction of hydrogen occurs at the cathode surface and a pH value increases. Along with the increase of the pH value, the stability of at least one metal element selected from the group consisting of Ti, Zr, Hf and Si is deteriorated and a surface treated film forms as a hydroxide containing oxide or water.

**[0037]** In the case of this electrolysis treatment, it is desirable that  $K=A/B$ , which is the ratio between total mole weight A of metal elements of Ti, Zr, Hf and Si and mole weight B which when total fluorine in fluorine containing compound is converted to HF, is  $K \leq 0.167$ . In the case of cathode electrolysis treating, since etching reaction of the metal material to be treated does not occur and surface treated film forms by reductive reaction, there is no lower limit of K. While, when K is larger than 0.167, since it is possible that the precipitating reaction occurs not only at the cathode surface but also in bulk surface treating solution along with the pH value elevating phenomenon by electrolysis, it is better to avoid the electrolysis treatment over the upper limit of K.

**[0038]** The present invention is to make it possible to remarkably improve the corrosion resistance of metal material by forming surface treated film layer composed of oxide and/or hydroxide of an metal element selected from the group consisting of Ti, Zr, Hf and Si on the surface of metal material. Oxide and/or hydroxide of said metal has a chemical property which has high resistance against acid or alkali and is chemically stabilized. At the actual corrosive environment of metal, at an anode, where solving out of metal occurs, the pH value is reducing and at the cathode, where reductive reaction of hydrogen occurs, the pH value is elevating. Therefore, in the case of a surface treated film which is inferior at acid resistance and alkali resistance, the film is dissolved under the corrosive environment and the effect of it is lost. Since the main component of the surface treated film layer of the present invention is not easily dissolved by acid or alkali, the excellent effect of the film can be maintained even under the corrosive environment.

**[0039]** Since oxide and hydroxide of said metal element forms a network structure through metal and oxygen, it can be an excellent barrier film. Although the state of corrosion changes along with the environment in which the film is used, ordinary, the corrosion is an oxygen demand type in the presence of water and oxygen, and the corrosive speed is promoted by the presence of chloride. Since the surface treated film layer of the present invention has a good barrier effect against water, oxygen and a corrosion promotion component, it can perform an excellent corrosion resistance.

**[0040]** For the purpose to enhance the corrosion resistance of iron metal material such as cold rolled steel plate, hot rolled steel plate, cast iron or sintered steel using above mentioned barrier effect, the adhered amount over than 30 mg/m<sup>2</sup> converted into said metal element is necessary, desirably is the adhered amount of over than 40 mg/m<sup>2</sup> and more desirable is the adhered amount of over than 50 mg/m<sup>2</sup>. And for the purpose to enhance the corrosion resistance of zinc metal material such as zinc, zinc plated steel plate or galvanized steel plate, the adhered amount over than 20 mg/m<sup>2</sup> converted into said metal element is necessary, desirably is the adhered amount of over than 30 mg/m<sup>2</sup>. Referring to the adhered amount, there is no upper limit, however, when the amount exceeds 1g/m<sup>2</sup>, cracks easily generate on the surface treated film layer and it becomes difficult to form an uniform film. Therefore, both in cases of iron metal material and zinc metal material, the desirable upper limit of adhered amount is 1g/m<sup>2</sup> and more desirably is 800 mg/m<sup>2</sup>.

#### EXAMPLE

**[0041]** The composition for surface treatment, the treating solution for surface treatment and the method for surface treatment of the present invention will be illustrated more readily in according to the Examples and Comparative Examples, however, not intended to restrict the scope of the claims of the present invention. And a material to be treated, a degreasing agent and a coating are voluntarily selected among the materials which are on the market, and not intending to restrict the actual uses of the composition for surface treatment, the treating solution for surface treatment and the method for surface treatment of the present invention.

[Test plate]

**[0042]** The abbreviation marks and details of the test plates used in Examples and Comparative Examples are shown as follows.

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- SPC: cold rolled steel plate (JIS-G-3141)
- GA: both side galvanized alloy zinc plated steel plate (45g/m<sup>2</sup>)
- Al: aluminum alloy plate (6000 type aluminum alloy)
- Mg: magnesium alloy plate (JIS-H-4201)

[Treating process]

**[0043]** Examples and Comparative Examples except zinc phosphate treatment are treated by following process.  
alkali degreasing → rinsing by water → film forming treatment → rinsing by water → rinsing by D.I. water → drying

**[0044]** Zinc phosphate treatment in Comparative Example is treated by following process.

alkali degreasing → rinsing by water → surface conditioning → zinc phosphate treatment → rinsing by water → rinsing by D.I. water → drying

**[0045]** Coating chromate treatment in Comparative Examples is treated by following process.

alkali degreasing → rinsing by water → rinsing by D.I. water → drying → coating of chromate treatment solution → drying

**[0046]** In Examples and Comparative Examples, the alkali degreasing is carried out as follows. That is, Fine Cleaner L4460 (T.M.: Product of Nihon Parkerizing) is diluted to 2% concentration by city water, and is sprayed to a plate to be plated at 40°C for 120sec.

**[0047]** The rinsing by water and rinsing by D.I. water after film treatment is carried out by spraying water or D.I. water to a plate to be plated at the room temperature for 30sec.

Example 1

**[0048]** Aqueous solution of titanium sulfate (IV) and hydrofluoric acid are used, and the composition for surface treatment whose mole weight ratio K of Ti and HF is 0.16 and Ti concentration is 2g/L is prepared. The obtained composition for surface treatment is diluted by D.I. water, then NaHF<sub>2</sub> reagent and NaOH reagent are added, and the treating solution for surface treatment whose K is 0.06, Ti mole concentration is 10 mmol/L and pH is 2.8 is prepared. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter (product of TOA Electronics Ltd.: IM-55G), and the result is 510ppm.

**[0049]** After degreased, the test plate is rinsed by water and is set up as a cathode. A carbon electrode is used as an anode, and the surface treatment by electrolysis is carried out for 5 sec at 5A/dm<sup>2</sup> electrolysis condition in above mentioned treating solution for surface treatment heated to the temperature of 35°C.

Example 2

**[0050]** Aqueous solution of hexafluorotitanic acid (IV) and hydrofluoric acid are used, and the composition for surface treatment whose mole weight ratio K of Ti and HF is 0.06 and Ti concentration is 1g/L is prepared. The obtained composition for surface treatment is diluted by D.I. water, then aqueous solution of titanium sulfate (IV) is added, and the solution whose K is 0.16 and Ti mole concentration is 0.05 mmol/L is prepared, and further 50ppm of HBrO<sub>3</sub> reagent is added. Thus the treating solution for surface treatment is prepared.

**[0051]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 40°C and surface treatment is carried out for 90 sec.

Example 3

**[0052]** Aqueous solution of hexafluorozirconic acid (IV), aqueous solution of zirconiumnitrate (IV) and hydrofluoric acid are used, and the solution whose mole weight ratio K of Zr and HF is 0.18 and Zr mole concentration is 50 mmol/L is prepared. Further, 5000ppm of NaNO<sub>3</sub> reagent and water soluble acrylic polymer compound (AC-10L: product of Nihon Jyunnyaku) is added so as the solid concentration to be 1%, and the treating solution for surface treatment is prepared.

**[0053]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 50°C and surface treatment is carried out for 60 sec.

Example 4

**[0054]** Aqueous solution of zirconiumnitrate (IV), aqueous solution of hexafluorosilicic acid (IV) and NH<sub>4</sub>F reagent are used, and the solution of mole ratio of Zr and Si is 1:1, mole weight ratio K of total mole weight of Zr and Si and HF is 0.08 and total mole concentration of Zr and Si is 100mmol/L is prepared. To the obtained solution, 150ppm of HClO<sub>3</sub> reagent and 50ppm of H<sub>2</sub>WO<sub>4</sub> reagent are added, thus the treating solution for surface treatment is prepared.



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**[0055]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 30°C and surface treatment is carried out for 90 sec.

### Example 5

**[0056]** Aqueous solution of titanium sulfate (IV) and hydrofluoric acid are used, and the composition for surface treatment whose mole weight ratio K of Ti and HF is 0.16 and Ti concentration is 2g/L is prepared. The obtained composition for surface treatment is diluted by city water, then  $\text{NaHF}_2$  reagent is added, and the treating solution for surface treatment whose K is 0.03, Ti mole concentration is 1 mmol/L is prepared. Further, to the obtained solution 300ppm as Ag of  $\text{AgNO}_3$  reagent and NaOH reagent are added and the treating solution for surface treatment whose pH is 3.5 is obtained. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter, and the result is 250ppm.

**[0057]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 45°C and surface treatment is carried out for 120 sec.

### Example 6

**[0058]** Aqueous solution of hexafluorotitanic acid (IV) and hydrofluoric acid are used and the composition for surface treatment whose mole weight ratio K of Ti and HF is 0.03 and Ti concentration is 10g/L is prepared. The obtained composition for surface treatment is diluted by city water, then aqueous solution of titanium sulfate (IV) is added, and the solution whose K is 0.167 and Ti mole concentration is 100 mmol/L is prepared, and further 50ppm of  $\text{HBrO}_3$  reagent, 15ppm as Al of  $\text{Al(NO}_3)_3$  reagent, 10ppm as Fe of  $\text{Fe(NO}_3)_3$  reagent and aqueous solution of ammonia are added. Thus the treating solution for surface treatment whose pH is 4.1 is prepared. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter, and the result is 30ppm.

**[0059]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 50°C and surface treatment is carried out for 60 sec.

### Example 7

**[0060]** Aqueous solution of hexafluorozirconic acid (IV) and  $\text{NH}_4\text{F}$  reagent are used, and the solution whose mole weight ratio K of Zr and HF is 0.1 and Zr mole concentration is 1 mmol/L is prepared. Further, 100ppm of  $\text{NaNO}_2$  reagent, 2000ppm as Mg of  $\text{Mg(NO}_3)_2$  reagent and aqueous solution of ammonia are added and the treating solution for surface treatment whose pH is 4.5 is prepared. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter, and the result is 5ppm.

**[0061]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 40°C and surface treatment is carried out for 90 sec.

### Example 8

**[0062]** Aqueous solution of hexafluorozirconate (IV) and hydrofluoric acid are used and the composition for surface treatment whose mole weight ratio K of Zr and HF is 0.15 and Zr concentration is 20g/L is prepared. The obtained composition for surface treatment is diluted by city water, then  $\text{NH}_4\text{F}$  reagent is added and the solution whose K is 0.08 and Zr mole concentration is 10mmol/L is prepared. Further, 5ppm Cu of  $\text{Cu(NO}_3)_2$  reagent, 100ppm as Mn of  $\text{Mn(NO}_3)_2$  reagent, 1500ppm as Zn of  $\text{Zn(NO}_3)_2$  reagent and aqueous solution of ammonia are added and the treating solution for surface treatment whose pH is 3.0 is prepared. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter, and the result is 200ppm.

**[0063]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment of 35°C and applied to the surface by spray for 120 sec., thus the surface treatment is carried out.

### Example 9

**[0064]** Hafnium fluoride and hydrofluoric acid are used and the solution whose mole weight ratio K of Hf and HF is 0.15 and Hf mole concentration is 0.05 mmol/L is prepared. Further, 1ppm Cu of  $\text{Cu(NO}_3)_2$  reagent, 100ppm of  $\text{H}_2\text{MoO}_4$  reagent, 10ppm of 35%- $\text{H}_2\text{O}_2$  aqueous solution and aqueous solution of ammonia are added and the treating solution for surface treatment whose pH is 5.0 is prepared. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter, and the result is 1ppm.

**[0065]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment of 40°C and applied to the surface by spray for 120 sec., thus the surface treatment is carried out.

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### Example 10

**[0066]** Aqueous solution of hexafluorosilicic acid (IV) and hydrofluoric acid are used, and the composition for surface treatment whose mole weight ratio K of Si and HF is 0.14 and Si concentration is 10g/L is prepared. The obtained composition for surface treatment is diluted by city water and adjust the Si mole concentration to 50 mmol/L, after that, 50ppm Ni of  $\text{Ni}(\text{NO}_3)_2$  reagent, 800ppm as Co of  $\text{Co}(\text{NO}_3)_2$  reagent, 15ppm of  $\text{H}_2\text{MoO}_4$  reagent, 50ppm of  $\text{HVO}_3$  reagent are added, and adjust the pH of solution to 5.9 by further adding aqueous solution of ammonia. Moreover, 2g/L of polyoxyethylenenonylphenylether (addition mole numbers of ethylene oxide: 12 moles), which is nonion surface active detergent, is added and the treating solution for surface treatment is prepared. The free fluorine ion concentration in this treating solution for surface treatment is measured by Fluorine Ion Meter, and the result is 500ppm.

**[0067]** The test plate is not degreased, then soaked into the obtained treating solution for surface treatment of 50°C and applied to the surface by spray for 90 sec., thus the surface treatment is carried out.

### Comparative Example 1

**[0068]** Aqueous solution of titanium sulfate (IV) and hydrofluoric acid are used, and the composition for surface treatment whose mole weight ratio K of Ti and HF is 0.1 and Ti concentration is 5g/L is prepared. The obtained composition for surface treatment is diluted by D.I. water, then  $\text{NaHF}_2$  reagent is added, and the treating solution for surface treatment whose K is 0.02 and Ti mole concentration is 90 mmol/L is prepared.

**[0069]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment heated to the temperature of 50°C and surface treatment is carried out for 120 sec.

### Comparative Example 2

**[0070]** Aqueous solution of hexafluorozirconic acid (IV) and  $\text{NH}_4\text{F}$  reagent are used, and the solution whose mole weight ratio K of Zr and HF is 0.17 and Zr mole concentration is 0.02 mmol/L is prepared.

**[0071]** The test plate is rinsed by water after degreased, then soaked into the obtained treating solution for surface treatment of 45°C and applied to the surface by spray for 120 sec., thus the surface treatment is carried out.

### Comparative Example 3

**[0072]** Alchrom 713 (T.M.: product of Nihon Parkerizing Co., Ltd.), which is the chromic chromate treating agent on the market, is diluted by city water to 3.6% concentration, then total acidity and free acid acidity are adjusted to the center value disclosed in the brochure.

**[0073]** The test plate is rinsed by water after degreased, then soaked into said chromate treating solution heated to the temperature of 35°C and chromate treatment is carried out for 60 sec.

### Comparative Example 4

**[0074]** Palcoat 3756 (T.M.: product of Nihon Parkerizing Co., Ltd.), which is the chrome free treating agent on the market, is diluted by city water to 2% concentration, then total acidity and free acid acidity are adjusted to the center value disclosed in the brochure.

**[0075]** The test plate is rinsed by water after degreased, then soaked into said chrome free treating solution heated to the temperature of 40°C and chrome free treatment is carried out for 60 sec.

### Comparative Example 5

**[0076]** The test plate is rinsed by water after degreased, then the solution prepared by diluting Prepalene ZN (T.M.: product of Nihon Parkerizing Co., Ltd.), which is a surface conditioning agent, by city water to 0.1% concentration is sprayed at the room temperature for 30 sec. Palbond L3020 (T.M.: product of Nihon Parkerizing Co., Ltd.) is diluted to 4.8% concentration by city water, and total acidity and free acidity are adjusted to the center value disclosed in the brochure. Thus the zinc phosphate treating solution is prepared. Above mentioned test plate is soaked into said zinc phosphate chemical treating solution heated to the temperature of 42°C, and zinc phosphate film is formed.

### Comparative Example 6

**[0077]** Zinchrom 1300AN (T.M.: product of Nihon Parkerizing Co., Ltd.) is diluted by D.I. water and coated using a bar coater and dried so as to the amount of Cr to be 30mg/m<sup>2</sup>.

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**[0078]** Each test plates whose surface are treated in above mentioned Examples and Comparative Examples are evaluated according to following items. That is, evaluation of appearance of surface treated film, amount of surface treated film layer, corrosion resistance of surface treated film layer and coating performance.

**[0079]** The appearance of surface treated plate by visual inspection. Results for appearance evaluation of surface treated film are summarized in table 1.

Table 1

	Appearance after surface treatment				
	SPC	GA	EG	Al	Mg
Example 1	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 2	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 3	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 4	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 5	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 6	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 7	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 8	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 9	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Example 10	U.I.C.	U.G.B.	U.G.B.	U.W.C.	U.W.C.
Comparative Example 1	uneven	uneven	uneven	white, uneven	white, uneven
Comparative Example 2	N.F.	N.F.	N.F.	F.N.F.	F.N.F.
Comparative Example 3	N.F.	S.Y.	S.Y.	G.C.	G.C.
Comparative Example 4	N.F.	N.F.	N.F.	W.U.	white, uneven
Comparative Example 5	G.U.	G.U.	G.U.	white, uneven	white, uneven
Comparative Example 6	uniform	uniform	uniform	uniform	uniform
In table 1, the meaning of each abbreviated codes are indicated as follows; U.I.C.: uniform interference color, U.G.B.: uniform grayish black color, U.W.C.: uniform white color, G.U.: grayish uniform, N.F.: not formed, F.N.F.: film is not formed, G.C.: golden color, S.Y.: slightly yellowish					

**[0080]** As shown in table 1, in Examples, uniform film is obtained on each test plates. On the contrary, in Comparative Examples, uniform film can not be formed.

**[0081]** The amount of surface treated film layer of surface treated plates are obtained in above mentioned Examples and Comparative Examples. At the measurement, an X-ray fluorescence analyzer (product of Rigaku Electric Industries: system 3270) is used, and elements in film are quantitatively analyzed, and calculated. The results are summarized in Table 2.

Table 2

	Amount of surface treated film layer (Total amount of Ti, Zr, Hf and Si: mg/m <sup>2</sup> )		
	SPC	GA	EG
Example 1	32	21	25

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Table 2 (continued)

	Amount of surface treated film layer (Total amount of Ti, Zr, Hf and Si: mg/m <sup>2</sup> )		
	SPC	GA	EG
Example 2	36	22	30
Example 3	81	45	58
Example 4	62	33	38
Example 5	52	28	36
Example 6	88	51	62
Example 7	72	48	61
Example 8	133	61	65
Example 9	115	55	59
Example 10	158	67	69
Comparative Example 1	25	13	18
Comparative Example 2	Trace	Trace	Trace
Comparative Example 3	Trace	Cr 35	Cr 45
Comparative Example 4	Trace	Trace	Trace
Comparative Example 5	Coating weight 2.3 g/m <sup>2</sup>	Coating weight 4.5 g/m <sup>2</sup>	Coating weight 2.1 g/m <sup>2</sup>
Comparative Example 6	Cr 31	Cr 32	Cr 32

**[0082]** As shown in Table 2, in all cases of Example, the aimed adhering weight to the test plates can be obtained. While, in Comparative Examples 1 and 2, the adhering amount within the scope of the present invention can not be obtained.

[Evaluation for corrosion resistance of the surface treated film layer]

**[0083]** 5%-NaCl aqueous solution is applied to the surface treated plate obtained in Examples and Comparative Examples by spray (in the case of SPC: 2hours, in the case of zinc plated steel plate: 24hours), the rust generated area after spray (SPC: red rust, zinc plated steel plate: white rust) is evaluated according to the following evaluation standard. The results of evaluation for corrosion resistance of the surface treated film layer are summarized in Table 3.

**[0084]** Rust generated area

Less than 5%	◎
Over than 5%, less than 10%	○
Over than 5%, less than 20%	△
Over than 20%	×

Table 3

	Corrosion resistance of surface treated film layer		
	SPC	GA	EG
Example 1	○	◎	◎
Example 2	○	◎	◎
Example 3	◎	◎	◎
Example 4	◎	◎	◎
Example 5	◎	◎	◎

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Table 3 (continued)

	Corrosion resistance of surface treated film layer		
	SPC	GA	EG
Example 6	⊙	⊙	⊙
Example 7	⊙	⊙	⊙
Example 8	⊙	⊙	⊙
Example 9	⊙	⊙	⊙
Example 10	⊙	⊙	⊙
Comparative Example 1	×	Δ	Δ
Comparative Example 2	×	Δ	Δ
Comparative Example 3	×	○	○
Comparative Example 4	×	×	×
Comparative Example 5	Δ	Δ	Δ
Comparative Example 6	×	⊙	⊙

**[0085]** As shown in Table 3, all Examples display good corrosion resistance to each test plate. On the contrary, in the cases of Comparative Examples 1 and 2, the corrosion resistance are inferior to that of Examples, because the adhering amount is smaller than the lower limit of the scope of claim of the present invention. In the case of Comparative Example 3, since it is chromate treating agent, the corrosion resistance for GA and EG is comparatively good, however, the corrosion resistance for SPC is very bad. Since Comparative Example 4 is a chrome free treating agent for aluminum alloy, sufficient corrosion resistance for SPC, GA and EG can not be obtained. Comparative Example 5 is a zinc phosphate treating agent, which is usually used as the substrate for coating, however, the result is inferior to that of Examples. Further, since the Comparative Example 6 is the coating type chromate treating agent for zinc plated steel plate, it displays good results to GA and EG, which are zinc plated steel plate, however, the result on SPC is inferior to Examples.

[Evaluation of coating performance]

(1) Preparation of evaluation plate

**[0086]** For the purpose to evaluate the coating performance of surface treated plates obtained in Examples and Comparative Examples, coating is carried out by following process.

cathodic electrodeposition coating → rinsing by D.I. water → baking → surfacer → baking → top coating → baking

- cathodic electrodeposition coating: epoxy type cathodic electrodeposition coating (Elecron 9400: product of Kansai Paint), electric voltage is 200V, thickness of film is 20 μm, baked at 175°C for 20 minutes.
- surfacer: aminoalkyd coating (AmilacTP-37 gray: product of Kansai Paint), spray coating, thickness of film is 35 μm, baked at 140°C for 20 minutes.
- top coating: aminoalkyd coating (AmilacTM-37 white: product of Kansai Paint), spray coating, thickness of film is 35 μm, baked at 140°C for 20 minutes.

(2) Evaluation of coating performance

**[0087]** The coating performance of surface coated plates whose surface is coated by above mentioned process. Evaluation items, evaluation method and abbreviation marks are shown below. Hereinafter, the coated film after electrodeposition coating process is called as electrodeposition coated film and the coated film after top coating is called as 3 coats coated film.

① SST: salt spray test (electrodeposition coated film)

**[0088]** To an electrodeposition coated plate to which cross cut line is marked by a sharpened knife, aqueous solution of 5%-NaCl is sprayed for 840 hours (in accordance with JIS-Z-2371). After sprayed, the maximum blistering width

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from both side of the cross cut line is measured.

② SDT: warm salt water dipping test (electrodeposition coated film)

**[0089]** An electrodeposition coated plate to which cross cut line is marked by a sharpened knife is soaked into aqueous solution of 5%-NaCl elevated to the temperature of 50°C for 240 hours. After, rinsed by city water and dried in room temperature, the cross cut part of electrodeposition coated film is peeled using a cellophane tape, and the maximum peeled width from both side of the cross cut part is measured.

③ 1st ADH: primary adhesion (3 coats coated film)

**[0090]** 100 checker marks of 2mm interval are marked using a sharpened knife on a 3 coats coated film. The checker mark part is peeled using a cellophane tape, and numbers of peeled checker mark are counted.

④ 2nd ADH: water resistant secondary adhesion (3 coats coated film)

**[0091]** A 3 coats coated film is soaked in D.I. water of 40°C for 240 hours. After soaked, 100 checker marks of 2mm interval are marked using a sharpened knife on it. The checker mark part is peeled using a cellophane tape, and numbers of peeled checker mark are counted.

⑤ CCT: cyclic corrosion test

**[0092]** A 3 coats coated film to which cross cut line is marked by a sharpened knife is placed into a complex environmental cycle testing apparatus and 60 cycles of following cycle test are repeated. Salt water spray (5%-NaCl, 50°C, 27hours) → drying (50°C, 3hours) → salt water soaking (5%-NaCl, 50°C, 2hours) → air-drying (25 °C , 2hours). After 60 cycles, the maximum blistering width from the cross cut part is measured and evaluated according to the evaluation standard indicated as follows.

Both side maximum blistering width

Less than 3mm	◎
Over than 3mm, less than 5mm	○
Over than 5mm, less than 10mm	△
Over than 10mm	×

**[0093]** Evaluation of coating performance of electrodeposition coated film are summarized in Table 4.

Table 4

	coating performance of electrodeposition coated film					
	SST			SDT		
	SPC	GA	AI	SPC	GA	AL
Example 1	4	5.2	0.5	3.1	4.5	0.5
Example 2	4	5	0.3	3.6	4.9	0.5
Example 3	2.8	4.3	0.5	2.5	4	0.3
Example 4	3.7	4.7	0.5	3.1	5	0.5
Example 5	3.9	4.8	0.5	3.2	5.1	0.5
Example 6	2.5	4.1	0.3	2.4	4.2	0.3
Example 7	2.5	4	0.3	2.7	4	0.5
Example 8	2.8	4	0.5	2	3.8	0.3
Example 9	2.7	4	0.5	2.1	3.6	0.5
Example 10	2.5	3.9	0.3	2	3.6	0.3
Com. Exp. 1	10.0<	6.5	0.6	10.0<	6.2	1

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Table 4 (continued)

	coating performance of electrodeposition coated film					
	SST			SDT		
Com. Exp. 2	10.0<	10.0<	1.5	10.0<	10.0<	2.2
Com. Exp. 3	10.0<	6.7	0.5	10.0<	5.8	0.3
Com. Exp. 4	10.0<	8.5	0.6	10.0<	10.0<	0.8
Com. Exp. 5	3.7	5.5	0.5	6	5.8	1.2

[0094] As clearly understood from Table 4, Examples show good corrosive resistance to all test plates. On the contrary, in Comparative Example 1, since mole weight ratio K of Ti and HF is 0.02 and HF concentration is higher to that of Ti concentration in treating bath, the precipitation of surface treated film is not sufficient and thus the corrosion resistance is not so good. Further, in Comparative Example 2, since Zr concentration is 0.02 mmol/L and is not reached to the enough Zr concentration to form surface treated film, the corrosion resistance is not so good too. Because Comparative Example 3 is a chromate treating agent for aluminum alloy and Comparative Example 4 is a chrome free treating agent for aluminum alloy, the corrosion resistance of Al is good, but the corrosion resistance of other test plates are obviously inferior to that of Examples. Comparative Example 5 is a zinc phosphate treating agent, which is now usually used as the base for coating. However, also in Comparative Example 5, it is difficult to improve the corrosion resistance of all test plates.

[0095] Results of adhesion of 3 coated film are summarized in Table 5.

Table 5

	Coating performance of 3 coats coated film											
	1st ADH				2nd ADH				CCT			
	SPC	GA	Al	Mg	SPC	GA	Al	Mg	SPC	GA	Al	Mg
Example 1-Example 10	0	0	0	0	0	0	0	0	⊙	⊙	⊙	⊙
Com. Exp. 1	0	0	0	0	5	3	0	0	×	Δ	Δ	Δ
Com. Exp. 2	0	0	0	0	7	6	9	10	×	×	Δ	Δ
Com. Exp. 3	0	0	0	0	20	0	0	0	×	Δ	⊙	⊙
Com. Exp. 4	0	0	0	0	19	9	0	0	×	×	○	Δ
Com. Exp. 5	0	0	0	0	0	0	0	0	⊙	⊙	○	Δ

[0096] As clearly shown in Table 5, Examples show good adhesion to all test plates. Regarding to 1st ADH, good results are obtained to all Comparative Examples, however, regarding to 2nd ADH there is no level which shows good adhesion to all test plates except zinc phosphate treatment. Further, regarding to CCT evaluation results for 3 coats plate, Examples 1-10 show good corrosion resistance to all test plates. On the contrary, Comparative Example 1-5, it is not possible to improve corrosion resistance of all test plate.

[0097] From above mentioned results, it is obviously understood following facts. That is, the precipitation of surface treated film having good adhesion and corrosion resistance on the surface of SPC, GA, Al and Mg without changing treating bath and treating condition is possible only by using the surface treating composition, the treating solution for surface treatment and the surface treating method of the present invention. Further, in Comparative Example 5, the generation of sludge, which is the by-product of zinc phosphate treatment, is observed in the treating bath after surface treatment. However, in Examples of the present invention, the generation of sludge is not observed in any level.

## INDUSTRIAL APPLICABILITY.

[0098] The surface treating composition, the treating solution for surface treatment and the surface treating method of the present invention are the remarkably excellent technique, which was impossible by the conventional technique. That is, the present invention is using a treating solution not containing harmful component to the environment and makes it possible to form a surface treated film having excellent corrosion resistance after coated on a surface of a metal containing iron and/or zinc. Further, according to the present invention, the generation of sludge, which can not be avoided in the conventional zinc phosphate treatment, can be prevented. The present invention is useful, because

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it can be applied to the metal surface such as combined metal material composed of steel plate, zinc plated steel plate and aluminum alloy or magnesium alloy or to the surface of each metal alone. Further, since the present invention does not need a process for surface conditioning, it is possible to attempt the shortening of the treating process and the reduction of space.

### Claims

1. A composition for surface treatment of a metal containing iron and/or zinc, comprising component (A) and component (B);

(A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.06 \leq K \leq 0.18$ .

2. A composition for surface treatment of a metal containing iron and/or zinc, comprising component (A), component (B) and component (C);

(A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,  
(C) a compound containing at least one metal element selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.03 \leq K \leq 0.167$ .

3. A treating solution for surface treatment of a metal containing iron and/or zinc, which comprises component (A) and component (B);

(A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,  
wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.06 \leq K \leq 0.18$ , and the concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si is within the region of 0.05 to 100 m mol/L.

4. A treating solution for surface treatment of a metal containing iron and/or zinc, which comprises component (A), component (B) and component (C);

(A) a compound containing at least one metal element selected from the group consisting of Ti, Zr, Hf and Si,  
(B) a compound containing fluorine as a supplying source of HF,  
(C) a compound containing at least one metal element selected from the group consisting of Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn,

wherein, ratio  $K=A/B$  between total mole weight A of metal elements of Ti, Zr, Hf and Si in the compound of component (A) and mole weight B which when total fluorine atom in fluorine containing compound of component (B) is converted to HF is within the range of  $0.03 \leq K \leq 0.167$ , and the concentration of component (A) indicated by the total mole concentration of metal elements of Ti, Zr, Hf and Si is within the region of 0.05 to 100 m mol/L.

5. The treating solution for surface treatment of a metal of claim 4, wherein the blending amount of compound of component (C) is adjusted to the sufficient amount to make the free fluorine ion concentration measured by fluorine ion meter smaller than 500 ppm.



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6. The treating solution for surface treatment of a metal according to any one of claims 3 to 5, to which at least one compound selected from the group consisting of  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HMnO}_4$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{WO}_4$ ,  $\text{H}_2\text{MoO}_4$  and salts of these oxygen acids is further added.
- 5 7. The treating solution for surface treatment of a metal according to any one of claims 3 to 6, to which at least one kind of surface active agent selected from the group consisting of nonion surface active agent, anion surface active agent and cation surface active agent is further added, and the pH is adjusted within the range of 2 to 6.
- 10 8. The treating solution for surface treatment of a metal according to any one of claims 3 to 7, to which at least one kind of polymer component selected from the group consisting water soluble polymer compound and water dispersible polymer compound is further added.
- 15 9. A method for surface treatment of a metal containing iron and/or zinc **characterizing**, the cleaned surface of said metal by previous degreasing treatment is contacted with the treating solution for surface treatment of a metal according to any one of claims 3 to 8.
- 20 10. A method for surface treatment of a metal containing iron and/or zinc **characterizing**, using the cleaned surface of said metal surface by previous degreasing treatment as a cathode and treating by electrolysis in the treating solutions for surface treatment of a metal according to any one of claims 3 to 8.
- 25 11. A method used simultaneous as degreasing and surface treatment of a metal containing iron and/or zinc **characterizing**, carrying out the degreasing treatment of metal surface and the film forming treatment of metal surface by contacting the metal surface with the treating solution for surface treatment of a metal of claim 7.
- 30 12. A metal material having excellent corrosion resistance, possessing a surface treated film layer composed of oxide and/or hydroxide of at least one kind of metal element selected from the group consisting of Ti, Zr, Hf and Si, which is formed by the method for surface treatment according to any one of claims 9 to 11, on a surface of iron metal material, wherein the amount of said surface treated film layer is over than  $30\text{mg/m}^2$  by converted amount to said metal elements.
- 35 13. A metal material having excellent corrosion resistance, possessing a surface treated film layer composed of oxide and/or hydroxide of at least one kind of metal element selected from the group consisting of Ti, Zr, Hf and Si, which is formed by the method for surface treatment according to any one of claims 9 to 11, on a surface of zinc metal material, wherein the amount of said surface treated film layer is over than  $20\text{mg/m}^2$  by converted amount to said metal elements.
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/05860

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>7</sup> C23C22/34, 22/50, 22/53//B05D3/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup> C23C22/00-22/86, B05D3/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Toroku Jitsuyo Shinan Koho	1994-2002
Kokai Jitsuyo Shinan Koho	1971-2002	Jitsuyo Shinan Toroku Koho	1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 9320260 A1 (Henkel Corp.), 14 October, 1993 (14.10.93), Description, page 5, line 1 to page 15, line 26; Claims & JP 07-505447 A	1-13
Y	US 4338140 A (Hooker Chem. & Plastics Corp.), 06 July, 1982 (06.07.82), Description, column 1, lines 10 to 17; column 3, line 40 to column 16, line 37; Claims & JP 57-41377 A	1-13
Y	GB 2165165 A (Parker Chem. Co.), 09 April, 1986 (09.04.86), Full description; Claims & JP 61-91369 A	1-13

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"&amp;" document member of the same patent family

Date of the actual completion of the international search  
06 September, 2002 (06.09.02)Date of mailing of the international search report  
17 September, 2002 (17.09.02)Name and mailing address of the ISA/  
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP02/05860

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 04-341574 A (Nippon Paint Co., Ltd.), 27 November, 1992 (27.11.92), (Family: none)	1-13

Form PCT/ISA/210 (continuation of second sheet) (July 1998)